

# Interesting electronic and structural properties of $C_3P_4$

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## Abstract

We performed first-principles calculation on several possible polymorphs of  $C_3P_4$  to investigate the structural and electronic properties of hypothetical carbon phosphide solids. Our calculations predict that  $C_3P_4$  is metallic within LDA. Unlike  $C_3N_4$ , the calculations also predict that pseudocubic- $C_3P_4$  is the most energetically favored structure at zero pressure. Being also the densest structure at zero pressure, it is perhaps only possible to synthesize pseudocubic- $C_3P_4$ .

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## 1. Introduction

Intense research on carbon nitride began after an empirical model by Cohen [1] proposed carbon nitride as a new superhard material having bulk modulus exceeding that of diamond. Subsequent first-principles calculations on  $C_3N_4$  showed that several polymorphs of  $C_3N_4$  have bulk moduli comparable to that of diamond and that  $C_3N_4$  is a wide gap material [2–5]. Recent measurements of the properties of  $C_3N_4$  have shown that earlier first-principles calculations are consistent with experimental results [6,7]. Although  $C_3N_4$  was further postulated together with  $C_3P_4$  as hard materials made of light covalent elements [8], no research has yet been done on carbon phosphide.

Trend analysis of the electronic structures of  $C_3N_4$  together with that of group III nitrides and phosphides, particularly BN, BP, AlN, AlP, GaN and GaP, suggests that we may expect carbon phosphide to be a wide gap semiconductor with  $E_g > 2$  eV. These motivated experimental efforts to synthesize and characterize phosphorus doped diamond-like carbon (DLC) films, with the ultimate aim of producing a stable form of carbon

phosphide having potentially useful electronic properties [9].

In this study, we investigate the structural and electronic properties of a series of hypothetical carbon phosphide solids of composition  $C_3P_4$  using first-principles calculation.  $C_3P_4$  can be obtained by substituting N with P in  $C_3N_4$ . Assuming that C atoms are 4-fold coordinated with P atoms and P atoms are 3-fold coordinated to C atoms in  $C_3P_4$ , we have considered as prototype structures for  $C_3P_4$  those that have been identified for  $C_3N_4$  in [5]. Using first-principles total energy pseudopotential techniques, we examined the energetics and the band structure for each of these polymorphs.

## 2. Method

Our ground state total-energy calculations were carried out based on density functional theory (DFT) [10] within the local density approximation (LDA) for electron exchange and correlation as parametrized by Perdew and Zunger [11]. The Vanderbilt ultrasoft pseudopotentials [12,13] were used, allowing a moderate plane-wave basis set to be employed. The electronic wave functions were expanded in terms of plane waves up to an energy cutoff of 310 eV. Special  $k$  points

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generated according to Monkhorst–Pack scheme [14] were used for integration over the irreducible wedge of the Brillouin zone for each structure. We used 18  $k$  points for  $\alpha$ -C<sub>3</sub>P<sub>4</sub>, 36 for  $\beta$ -C<sub>3</sub>P<sub>4</sub>, 32 for cubic-C<sub>3</sub>P<sub>4</sub>, 32 for pseudocubic-C<sub>3</sub>P<sub>4</sub> and 16 for graphitic-C<sub>3</sub>P<sub>4</sub>. Good convergence was achieved with this cutoff energy and the number of  $k$ -points.

Each crystal geometry was optimized within the preselected space groups. We then computed the band structures for each polymorph. Assuming uniform compression and expansion of the lattice, we also

evaluated the total energy over a wide range of volume for each optimized structure. At a given volume, positions of the ions were determined by minimizing the forces on the ions within the preselected space groups.

### 3. Results and discussion

The calculated band structures for each C<sub>3</sub>P<sub>4</sub> polymorph as shown in Fig. 1(a)–(e) reveal that C<sub>3</sub>P<sub>4</sub> is

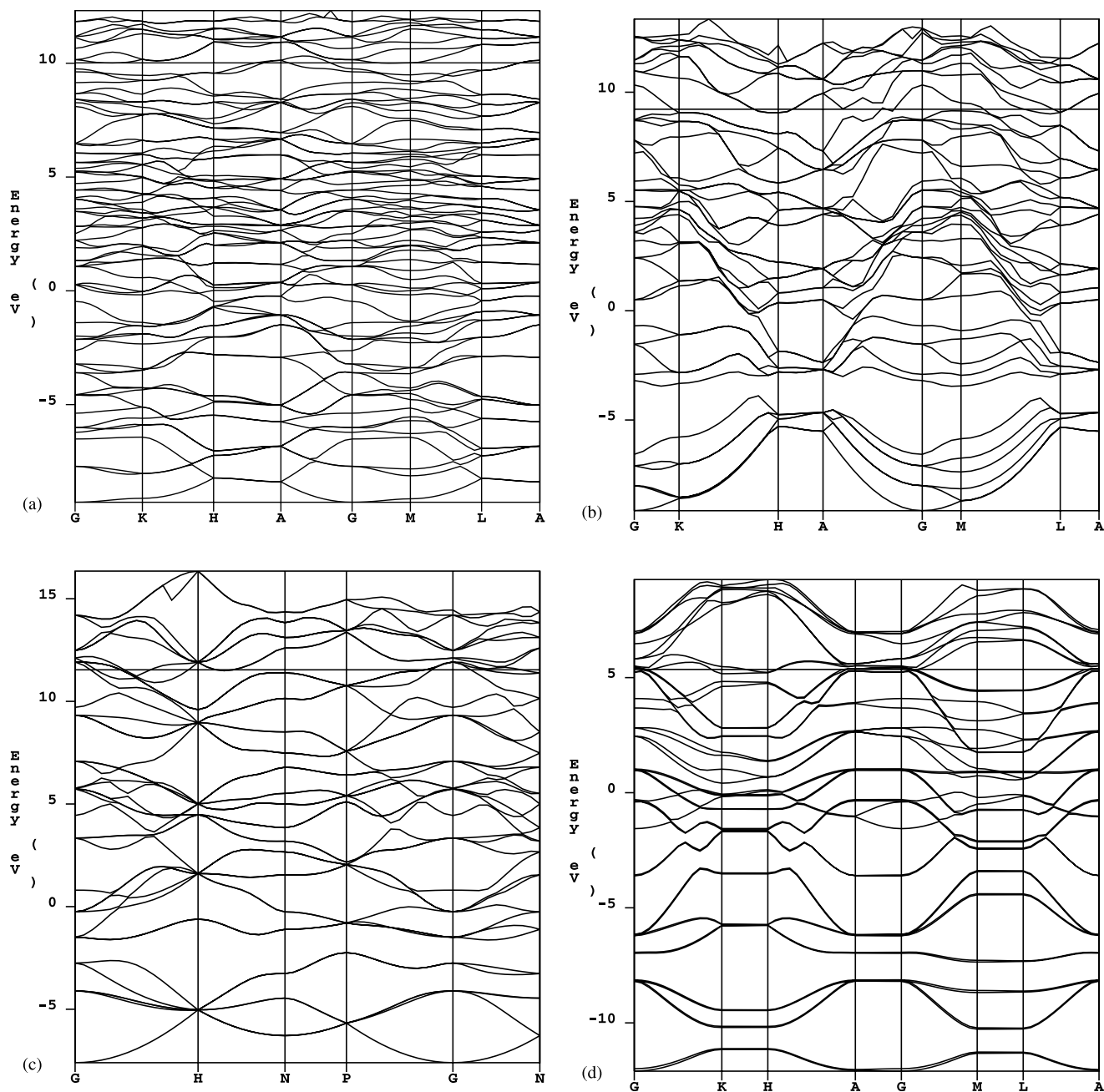


Fig. 1. Band structure for (a)  $\alpha$ -C<sub>3</sub>P<sub>4</sub>, (b)  $\beta$ -C<sub>3</sub>P<sub>4</sub>, (c) cubic-C<sub>3</sub>P<sub>4</sub>, (d) graphite-C<sub>3</sub>P<sub>4</sub> and (e) pseudocubic-C<sub>3</sub>P<sub>4</sub>. The horizontal line corresponds to the Fermi level,  $E_F$ . The calculated band structures for each C<sub>3</sub>P<sub>4</sub> polymorph reveal that C<sub>3</sub>P<sub>4</sub> is metallic within LDA.

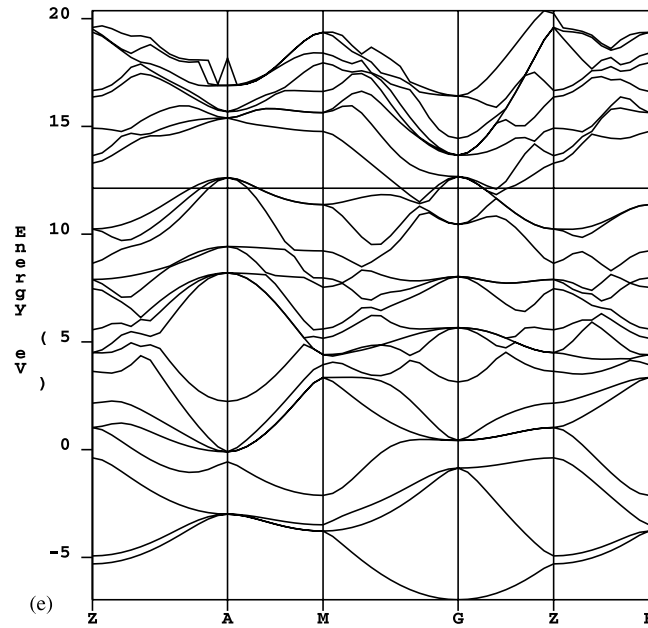


Fig. 1 (Continued)

Table 1  
Elemental electronegativities of C, N, and P in tetrahedrally coordinated environments [17]

Element	Electronegativity
C	2.50
N	3.00
P	1.64

metallic within LDA. Despite underestimating the band gap, it is rather well established that LDA reproduces reliable qualitative features of the band structures in the ground state. One approach to correct this shortcoming of LDA is to rigidly shift the conduction band upwards by a difference between the results obtained in a quasiparticle calculation and that obtained using LDA [15,16]. Nevertheless, because of significant overlap between the conduction and valence bands, it is still possible that  $C_3P_4$  is metallic at room temperature.

To compare our results for  $C_3P_4$  with that of  $C_3N_4$ , we repeated our calculations with  $\alpha$ - $C_3N_4$ ,  $\beta$ - $C_3N_4$ , cubic- $C_3N_4$ , pseudocubic- $C_3N_4$  and graphitic- $C_3N_4$ . Our calculations are in good agreement with earlier

first-principles calculations of  $C_3N_4$  which predicted wide band gaps for the polymorphs of  $C_3N_4$  considered in this study [5]. This indicates that the substitution of N by P in  $C_3N_4$  results in drastic changes in the electronic structure of  $C_3N_4$  although both N and P are group V elements.

This may be explained in terms of the electronegativities of C, N and P atoms. The electronegativities of C, N and P atoms are given in Table 1. Despite similarities in valency, N and P atoms differ in electronegativity. On the other hand, the electronegativity of C atom is greater than that of P atom but less than that of N atom. This will lead to a difference in the electronic bonding properties between the two solids. The difference between C–N and C–P bonds may be one of the possible reasons why  $C_3N_4$  is an insulator whereas  $C_3P_4$  is metallic. Since electronegativity describes the ability of an atom to attract electrons to itself, we may expect that the valence electrons of the C atoms to be attracted and tightly bound to the N atoms in  $C_3N_4$ . On the other hand, the electronegativity of P atom is less than that of C atom and hence the P atoms are more willing to give away electrons to the C atoms in  $C_3P_4$ .

Table 2  
Equilibrium structural parameters and total energies calculated for  $\alpha$ - $C_3P_4$ ,  $\beta$ - $C_3P_4$ , cubic- $C_3P_4$ , pseudocubic- $C_3P_4$  and graphitic- $C_3P_4$

	$\alpha$ - $C_3P_4$	$\beta$ - $C_3P_4$	Cubic- $C_3P_4$	Pseudocubic- $C_3P_4$	Graphitic- $C_3P_4$
Space group	$P3_1c$ (159)	$P6_3/m$ (176)	$I\bar{4}3d$ (220)	$P\bar{4}2m$ (111)	$P\bar{6}m2$ (187)
$a$ (Å)	8.1200	8.3193	6.6699	4.1016	5.7227
$c$ (Å)	5.7552	2.8148	–	4.1010	8.1684
$E_0$ (eV/ $C_3P_4$ unit)	–1185.0063	–1184.0092	–1183.5525	–1186.8014	–1184.2644

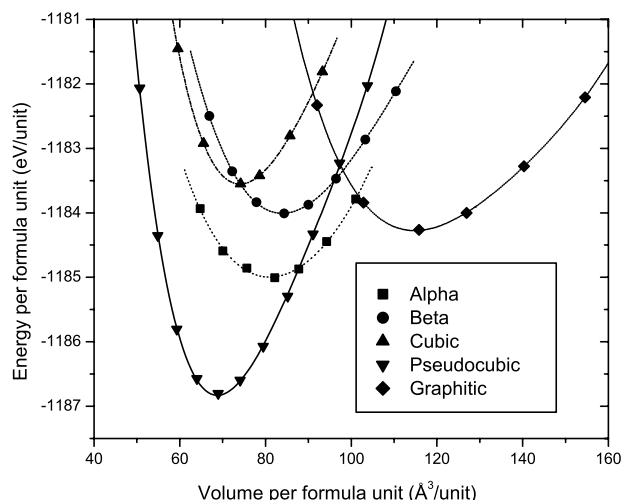


Fig. 2. The total energies per  $C_3P_4$  unit as a function of volume for the various structures considered.

Table 2 shows the equilibrium structural parameters and total energies per  $C_3P_4$  unit for each structure. The total energies per  $C_3P_4$  unit as a function of volume for the various structures considered are shown in Fig. 2. In contrast to  $C_3N_4$ , pseudocubic- $C_3P_4$  is energetically favored relative to  $\alpha$ - $C_3P_4$  and  $\beta$ - $C_3P_4$  over a wide range of volume. The calculations predict that the pseudocubic- $C_3P_4$  structure has the lowest energy at zero pressure. At zero pressure, the total energy per  $C_3P_4$  unit of the pseudocubic- $C_3P_4$  structure is 2 eV lower than the next most energetically favored structure, i.e.  $\alpha$ - $C_3P_4$ . As shown in Fig. 2, the pseudocubic- $C_3P_4$  structure is also predicted to have the highest density at zero pressure. These results are consistent with our previous evaluation of the equilibrium structural parameters and total energy curves [18]. In [18], the evaluation of the total energy curves was done without including the effects of atomic relaxation.

#### 4. Conclusion

Our results suggest that carbon phosphide with stoichiometry  $C_3P_4$  is metallic. This may be due to the electronegativity difference between N and P atoms relative to the C atom which leads to a difference in the electronic bonding properties between  $C_3N_4$  and  $C_3P_4$ . Because pseudocubic- $C_3P_4$  is the most energetically favored in addition to being the densest structure at zero pressure, it is perhaps only possible to synthesize pseudocubic- $C_3P_4$  among the various structures considered in this study.

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